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DRES

SUFFIELD MEMORANDUM

NO. 1074

**ASSESSMENT OF THE PERSISTENCE OF VAPOUR EVOLVED
FROM NEAT CH CONTAMINATION ON PRAIRIE TERRAIN (U)**

(Record of FPP 81-1)

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Stanley B. Mellisen

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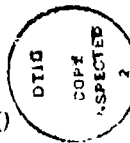
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ABSTRACT

A field experiment has been conducted to assess the persistence of CH when dispersed on prairie terrain. Explosive dissemination yielded liquid droplets of 0.1 mm mass median diameter. Ninety percent of the total vapour recovery occurred within four minutes and 88% of the disseminated chemical was recovered.

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INTRODUCTION

1. A requirement has been stated (1) by the Canadian Armed Forces for a training agent which will produce an inhalable, physiologically active vapour without persistence on surfaces. As the volatile liquid CH (a mixture of 1-methoxycycloheptatriene (EA 4923), 2-methoxycycloheptatriene, and 3-methoxycycloheptatriene (EA 4922)) shows promise of meeting these requirements, arrangements were made to conduct a field experiment (2) to assess its persistence on prairie terrain. Sufficient CH for a single trial was available.
2. Several trials are usually required to obtain sufficient data to accurately characterize an agent. However, the results of one trial are frequently useful if field conditions are good and the experimental apparatus performs well. Because this was the case in the first trial with CH, the results are reported here to provide early information on its field behavior.

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TRIAL OBJECTIVES

3. a. To contaminate explosively an area of prairie terrain, 24 m crosswind \times 16 m downwind, to a mean contamination density of 2 gm^{-2} with CH.
- b. To determine drop sizes and ground contamination densities from the explosive dissemination.
- c. To sample vapour return from the layout sequentially at heights from 0.3 m to 1.5 m above ground.

EXPERIMENTAL DETAILS

4. a. Material

- (1) A total of 1403 g of agent was used in the trial. As reported by CSL the material used contained 94.6% methoxycycloheptatrienes, 1.9% BHA + BHT as stabilizers (antioxidants) and 3.5% unidentified impurities. The isomer proportions for the methoxycycloheptatrienes fraction was found by nmr to be:

82.3% EA 4923

2.0% 2 methoxycycloheptatriene

15.6% EA 4922

- (2) Six 250 mL linear polyethylene bottles (Nalgene) were charged before the trial. The weights of CH in each separately were 231, 240, 227, 224, 232 and 249 g respectively. The screw cap of each bottle was modified to provide a well for a length of primacord. One hundred grains of primacord initiated by a No. 12 detonator was used in each bottle.

b. Layout

The sampling layout covered a 24 m \times 16 m rectangular area on the DRES Vertical Grid Site (Figure 1), with ground sampling positions

on a 2 m \times 3 m grid and four vapour sampling positions on the downwind edge. Gallows made of 1.5 cm diameter steel rod, with arms at 1 m and 2 m above the ground to support the bottles, were emplaced as indicated.

c. **Ground Contamination Sampling**

Sampling of drop sizes was carried out with 20 \times 30 cm sheets of 3-way detector paper mounted on jump cards while contamination densities were determined using pie plates, each containing 100 mL of diethyl succinate, which was used as an involatile solvent. Each pie plate, which was 8 inches in diameter, was covered with a flat topped ring with a 6 inch diameter circular hole in its center to collect the droplets falling into the horizontal plane. The ring for each plate was made so that a lip at the edge fitted loosely over the pie plate for easy removal. This was done to facilitate replacement with a tight fitting lid immediately after contamination to keep vapour from escaping. The samplers were placed on the ground on the layout to form the 2 m \times 3 m grid previously mentioned (Figure 1).

d. **Vapour Sampling**

Vapour samples were taken in bubblers charged with 2 mL diethyl succinate and aspirated at 1 L min⁻¹. Six sequential samples were taken at 0.3, 0.5, 1.0, and 1.5 m in height. Also four field blanks and four vapour slip tests were taken in the trial. Each vapour slip test consisted of two bubblers connected in series, so that the amount of material escaping from the first bubbler could be determined. A Miran 1-A infrared gas analyzer, equipped with a 20 m pathlength gas cell, was used to obtain vapour concentration in real time. The sampling probe for the analyzer was located at a height of 1 m.

e. **Meteorology**

Meteorological observations were made at a position crosswind from the layout. Windspeeds at 0.5, 1.0, 1.5 and 2.0 m above ground, wind direction at 2 m and ground temperatures were recorded for the duration of the sampling.

PROCEDURE5. a. **Layout**

The layout was oriented according to the expected 2 m wind direction of 210 T. Four field blank samples were taken before Zero and the infrared gas analyzer was started at Zero - 1 minute. The agent-charged bottles were armed and suspended at 1 m above ground from the gallows (Figure 2). At Zero the bottles were exploded electrically (Figure 3) and vapour sampling commenced. The rings were removed from the pie plates and replaced by tight fitting lids within two minutes after Zero (Figure 4). Then the pie plate samplers were gathered and placed in racks (Figure 5) and carried to a position upwind of the layout (Figure 6). The detector paper samplers were picked up after the vapour sampling was over, stacked in racks and allowed to dry before drop size analysis was attempted. The four vapour slip tests for bubblers were operated during the entire bubbler vapour sampling period.

b. **Zero**

1103 MDT: 26 April 1982

c. **Vapour Sampling Schedules**

Bubblers at 0.3, 0.5, 1.0 and 1.5 m

Position S1, S2, S3

Z to Z + ½ minute

Z + ½ to Z + 1 minute

Z + 1 to Z + 2 minutes

Z + 2 to Z + 6 minutes

Z + 6 to Z + 20 minutes

Z + 20 to Z + 40 minutes

Position S4

Z - 1 to Z + 40 or until vapour concentration becomes negligibly small in comparison to the peak concentration.

d. **Analysis**

The vapour samplers from the bubblers and the ground contamination samples were analyzed by gas chromatography and vapour dosages calculated. The total methoxycycloheptatriene fraction was analyzed for, and the vapour dosages and percent recovery are based on this analysis. Stain sizes on detector papers were measured and counted by a Quantimet System 23 image analysis system and analyzed mathematically for number-drop diameter distribution.

RESULTS

6. a. **Weather Conditions**

The weather was sunny and dry and the wind direction and speed were nearly constant during the entire period of the trial. Air and ground temperatures, windspeeds at various heights, and wind direction at 2 m are given in detail in Appendix A.

b. **Ground Contamination**

The agent arrived at the ground in the form of small discreet drops as indicated by a typical sampling card (Figure 7). The detailed drop sizing data for all trials is shown in Appendix B. These results are also plotted along with a fitted curve (Figure 8). The methods used in fitting the curve and obtaining the mass median diameter, which was found to be 0.10 mm, are also described in Appendix B. The detailed contamination density data is shown in Appendix C.

b. **Vapour Recovery**

Sequential vapour dosages at 0.3, 0.5, 1.0 and 1.5 m measured over the whole sampling period for each trial are given in Appendix D. Also shown is the mean cumulative vapour recovery to 1.5 m height obtained from the three bubbler sampling arrays. In the last sampling interval the mean recovery in all the previous sampling intervals indicating a very small residual dosage. The four field blanks showed

no vapour recovery. The bubbler slip tests showed an average slip of vapour through the first bubbler of 22.7%. Therefore, a correction factor of 1.227 was applied to all bubbler vapour sample results obtained from laboratory analysis. The correction factor was obtained from the average of the values for four pairs of test bubblers. It was calculated for each pair of test bubblers in the following way. The total vapour, V , which passes through the first bubbler is obtained from the ratio, r , of the recovery by the second bubbler to the recovery, a , of the first bubbler by a geometric progression of an infinite cascade with common recovery ratio r . The sum of the series is:

$$V = \frac{a}{1 - r} \quad (\text{Eq. 1})$$

Then the correction factor to be applied to the results of laboratory analysis of each sample is simply given by the following equation:

$$\frac{V}{a} = \frac{1}{1 - r} \quad (\text{Eq. 2})$$

The correction factor which was determined for each of the four slip test pairs is shown in Appendix D following the vapour dosage results. The vapour concentrations measured in real time by the infrared gas analyzer are shown in Appendix E. Integration of the concentration over the interval $Z + \frac{1}{2}$ min to $Z + 2$ min by the trapezoidal rule obtains a dosage of $31.82 \text{ mg min m}^{-3}$. The average dosage over the same time interval measured by the bubblers S1 and S2, between which the IR analyzer was located, was $28.66 \text{ mg min m}^{-3}$. Thus the results show good agreement.

d. **Agent Recovery Comparison**

- (1) Using a point count method in which each sample represented a $3 \times 2 \text{ m}$ area, the ground contamination was calculated in terms of weight per metre of crosswind width from the mean contamination density over the $18 \times 16 \text{ m}$

sampling area. The results are shown (Table I) along with the source strength and vapour recovery. As can be seen the ground recovery was only 31% of the source strength. Part of the reason for this is that some of the agent travelled directly from the explosively disseminated source to the vapour samplers without reaching the ground, which was due to the high volatility of the agent.

- (2) Vapour recovery, the integrated flux of agent through a 1 m crosswind width, was calculated from the vapour dosage and wind profile data. The results are given along with the ground contamination information (Table I).

TABLE I
Comparison of Measured Total Vapour
Recovery to Total Liquid Dispersed

TRIAL NO.	CHARGE (gr Primacord)	SOURCE STRENGTH (g gm ⁻¹)	RECOVERY ON LAYOUT			
			GROUND		VAPOUR	
			gm ⁻¹	%q	gm ⁻¹	%q
FPP81-1	100	48	15	31	42	88

c. Similarity of Experimental and Theoretical Recoveries

The time profile of vapour recovery has been shown to be predictable by means of a mathematical model (Monaghan and McPherson). If the rate of absorption into vegetation is equal for two agents, then the model shows that the time profiles of vapour recovery from liquid ground contamination are similar, and differences in volatility are reflected in a time normalizing parameter T .

Assuming that the material was not strongly absorbed by the substrate, which is a fair assumption due to the high vapour recovery (Table I) the actual recovery rate was compared to a theoretical curve for 90% recovery from the substrate, taking into account that some of the agent travelled directly to the vapour samplers without reaching the ground. With a recovery of 12.3 gm^{-1} directly from the dissemination, the data, adjusted to standard windspeed and temperature of 18 km hr^{-1} at 2 m and 20°C respectively, agree with the theoretical predictions reasonably well (Figure 9). The comparison is also shown in normalized form (Figure 10), using a value of T of 0.08 minutes derived using Figure 9. The mean liquid loading M of CH on the vegetation corresponding to this value of T was 19 gm^{-2} , which is what is normally expected based on previous experience with other agents such as triethylphosphate. Also the recovery from the ground samplers, when based on the difference between the amount disseminated and the amount which reached the vapour samplers without first contacting the ground, was 52%. This amount is in the realm of recovery in trials with triethylphosphate using a similar sampling layout. However, the losses could possibly have occurred for different reasons, since sponges were used instead of pie plates for ground contamination sampling in trials with triethylphosphate.

CONCLUSION

The explosive dissemination of CH yielded drops on the ground with a mass median diameter of 0.1 mm and some vapour which passes directly to the samplers. Ninety percent of the total vapour recovery took place within 4 minutes after dissemination and 88% of the total disseminated CH was recovered. This indicates that the persistence of CH disseminated as in this trial is so low that it can be treated essentially as an instantaneous vapour source, from the point of view of downwind hazard. The evaporation behavior of liquid CH from the ground was found to be similar to that of other agents which are not strongly absorbed by the vegetation.

REFERENCES

1. Anon. "Canadian Forces Statement of Requirement Preliminary – Training System for Chemical Defence". DOTC 2/78. RESTRICTED.
2. Mellsen, S.B. "Assessment of the Persistence of Vapour Evolved from Neat EA4923. Contamination on Prairie Terrain (U). (Procedures to be used in FPP 81)". Suffield Research Note No. 141. August 1981. RESTRICTED.
3. Monaghan, J. and W.R. McPherson. "A Mathematical Model for Predicting Vapour Dosages on and Downwind of Contaminated Grassland (U)". Suffield Technical Paper No. 286 1971. UNCLASSIFIED.

APPENDIX A

METEOROLOGICAL OBSERVATIONS

Field Experiment FPP 81Trial 1Date April 26/82Zero 1103 M.D.T.

TIME	DIRECTION	WIND PROFILE km hr ⁻¹				TEMPERATURES °C	
Z minutes	Deg T	½ m	1 m	1 ½ m	2 m	Air	Ground
+ ½	210	7.3	10.6	15.6	16.0	12.0	20.9
1	210	8.1	11.1	16.0	18.0	12.0	21.0
2	220	8.0	10.2	12.0	12.0	12.4	21.0
6	225	9.0	13.0	15.0	16.5	13.1	22.0
20	185	9.0	12.7	14.6	17.4	14.2	23.3
40	200	9.0	12.6	14.4	17.2	15.9	29.2
60	180	8.7	11.7	14.4	14.1	16.1	31.1
90	230	7.6	10.6	13.2	13.8	16.4	32.3

Wind speeds are means between the indicated times. All other data are spot readings.
The sun was bright and the surface of the ground was dry during the trial period.

APPENDIX B

DROP SIZE SAMPLING RESULTS

FPP 81 — TRIAL 1

STAIN SIZE	DROP SIZE	TOTAL NUMBER*
mm	mm	
0 — 0.15	—	—
0.15 — 0.3	0.084	10202
0.3 — 0.4	0.112	2072
0.4 — 0.5	0.130	1356
0.5 — 0.6	0.149	786
0.6 — 0.7	0.167	418
0.7 — 0.8	0.186	191
0.8 — 0.9	0.204	93
0.9 — 1.0	0.222	64
1.0 — 1.1	0.241	22
1.1 — 1.2	0.259	16
1.2 — 1.3	0.278	7
1.3 — 1.4	0.296	6
1.4 — 1.5	0.314	3
> 1.5	> 0.333	0

* The total number on 48 20 × 20 cm cards. Two fields, each containing 5024.0 mm² were measured by the Quantimet analyzer on each card

The data from this trial were found to follow the relationship

$$N = N_r \exp - bD \quad (\text{Eq. B1})$$

where N_r is the intercept at diameter $d = 0$, N is the cumulative number of drops and b is a constant. The mass median diameter D_0 of the distribution is related to b by the following equation:

$$bD_0 = 3.672 \quad (\text{Eq. B2})$$

Fitting the data to Equation B1 yielded the following results with a correlation coefficient $r^2 = 0.9995$:

$$N_r = 287026$$

$$b = 35.263$$

Using Equation B2 the mass median diameter, D_0 was calculated to be 0.10 mm.

APPENDIX C

CONTAMINATION DENSITY SAMPLES g m^{-2}

FPP 81 — TRIAL 1

ROW/LINE	1	2	3	4	5	6
H	0.01	0	0.02	0.01	0	0.02
G	0.02	0.19	0.88	0.31	0.05	1.62
F	0.33	0.65	2.45	1.97	1.08	0.37
E	0.46	1.37	2.20	3.58	1.15	6.37
D	0.46	2.65	1.49	2.35	0.85	1.01
C	0.52	1.43	1.32	0.86	0.83	0.52
B	0.59	1.39	1.13	0.74	0.48	0.48
A	0.46	1.28	0.47	0.77	0.40	0.36

Mean Contamination Density 0.96 g m^{-2} .

APPENDIX D

VAPOUR DOSAGE SAMPLES FROM BUBBLERS mg min m^{-3}

FPP 81 -- TRIAL 1

POSITION	HEIGHT M	SAMPLING INTERVAL (Minutes)					
		Z - Z + ½	Z + ½ - Z + 1	Z + 1 - Z + 2	Z + 2 - Z + 6	Z + 6 - Z + 20	Z + 20 - Z + 40
S1	0.3	202.07	59.31	19.08	19.39	12.69	4.39
	0.5	141.76	37.77	13.82	13.09	6.97	4.53
	1.0	72.87	18.37	10.80	9.24	5.24	4.67
	1.5	35.57	10.63	5.58	6.43	4.81	—
S2	0.3	198.75	59.65	29.41	20.55	8.80	4.16
	0.5	156.70	47.07	22.61	15.85	14.91	10.66
	1.0	59.82	16.81	11.33	7.79	3.88	—
	1.5	21.36	12.05	6.59	4.12	—	—
S3	0.3	214.77	36.28	16.14	13.83	8.50	3.28
	0.5	178.95	26.63	12.75	12.65	6.50	4.39
	1.0	99.19	10.99	7.60	8.77	4.40	3.98
	1.5	54.17	5.84	3.37	3.62	—	2.17

MEAN CUMULATIVE VAPOUR RECOVERY TO 1.5 m HEIGHT g m^{-1}

Z - Z + ½	Z + ½ - Z + 1	Z + 1 - Z + 2	Z + 2 - Z + 6	Z + 6 - Z + 20	Z + 20 - Z + 40
25.58	33.14	36.38	39.32	41.03	42.06

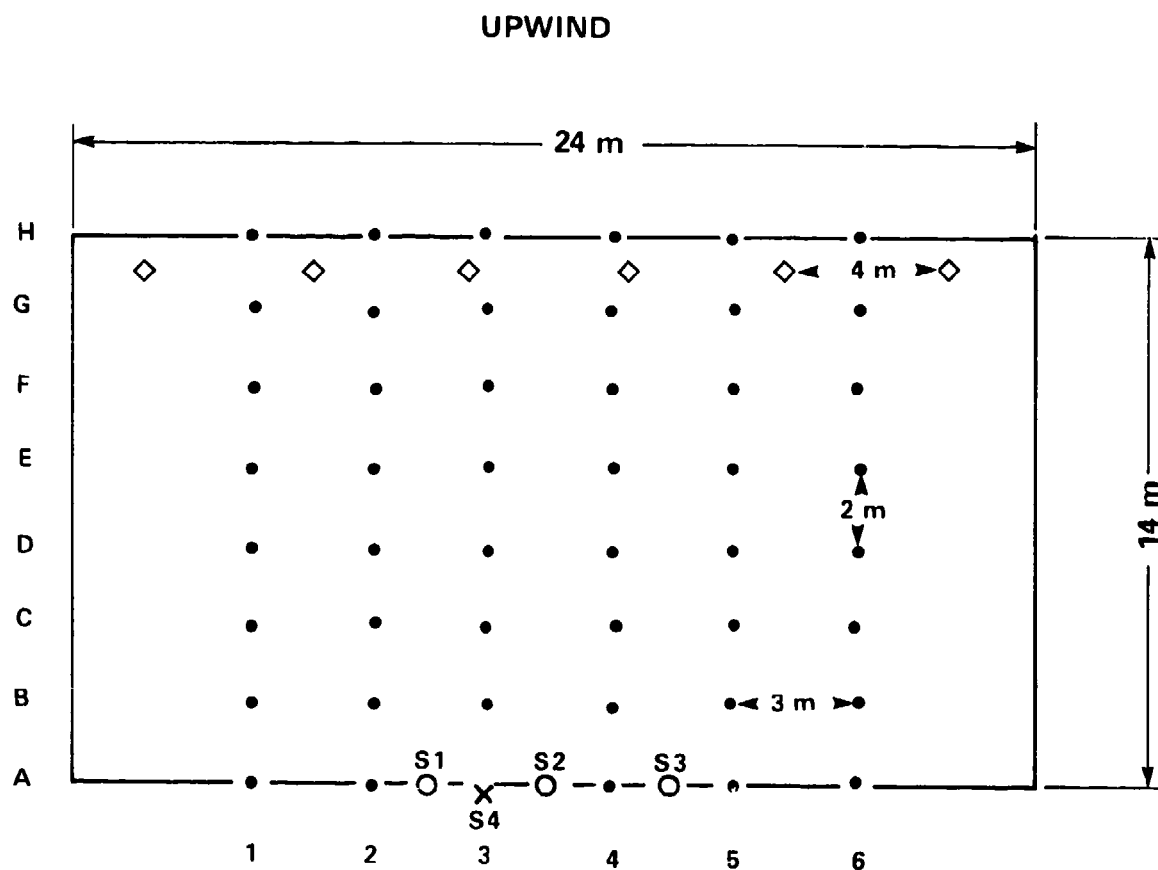
APPENDIX D (Cont'd)**BUBBLER SLIP TESTS**

PAIR NO.	CT mg min m ⁻³	PAIR RATIO	CORRECTION FACTOR
			$\frac{1}{1 - r}$
1	247.616 46.357	0.187	1.230
2	226.266 40.050	0.177	1.215
3	250.817 42.095	0.168	1.202
4	241.906 49.707	0.205	1.259
			Average Correction Factor 1.227

APPENDIX E

INFRARED GAS ANALYZER RESULTS

TRIAL TIME sec	CH CONCENTRATION mg m ⁻³
Z - 1	0
Z + 6	174.9
Z + 12	151.0
Z + 18	119.3
Z + 24	71.6
Z + 30	71.6
Z + 36	67.6
Z + 42	59.6
Z + 48	43.7
Z + 54	25.4
Z + 60	12.7
Z + 66	12.7
Z + 72	11.1
Z + 78	9.5
Z + 84	8.0
Z + 90	4.8
Z + 96	5.6
Z + 102	6.4
Z + 108	5.6
Z + 114	6.4
Z + 120	6.4
Z + 126	5.6
Z + 132	4.4
Z + 138	4.8
Z + 144	3.2
Z + 150	3.2



• Detector Paper and Pie Plate Samplers.

○ S1, S2, and S3. Bubblers at 0.3, 0.5, 1.0 and 1.5 m.

× S4 Infrared Gas Analyzer at 1.0 m.

◇ GZ of Bursting Bottles, Gallows Position.

Figure 1

LAYOUT DIAGRAM

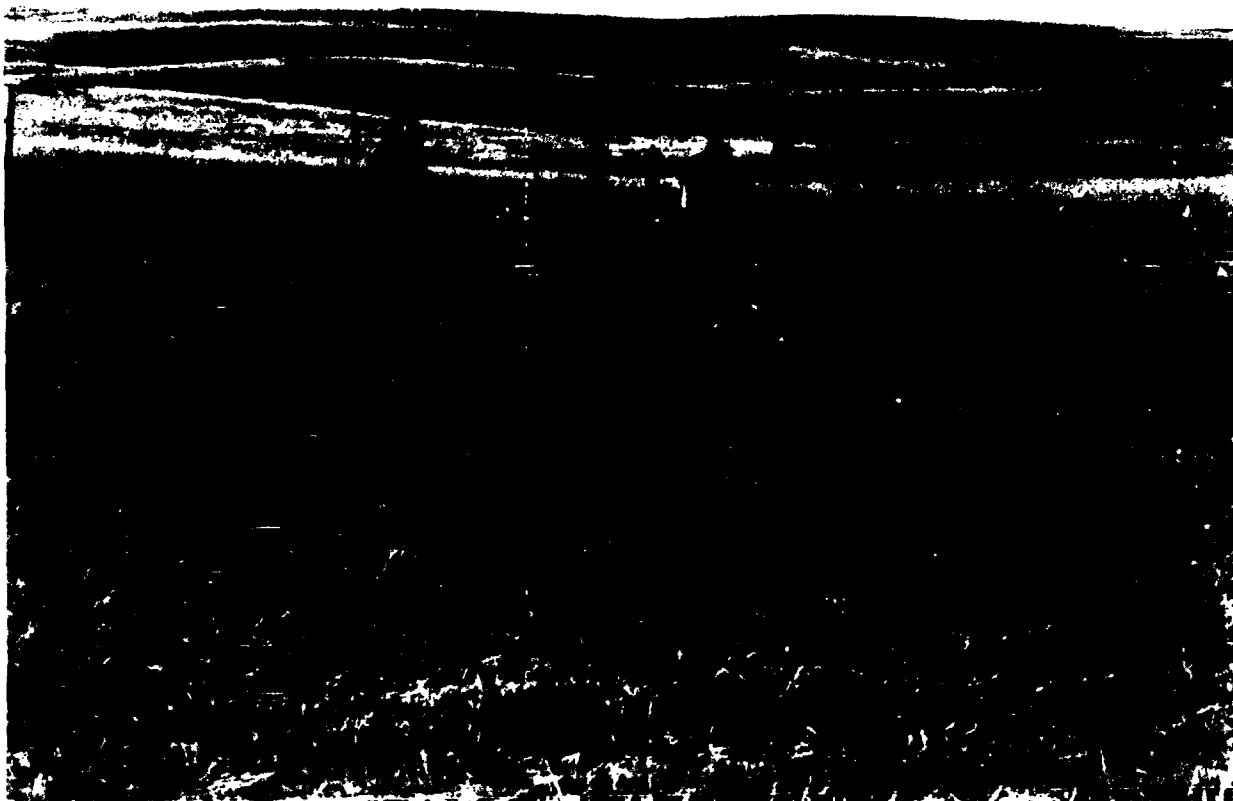


Figure 2

VIEW OF SAMPLING LAYOUT SHOWING BOTTLES
BEING SUSPENDED AT 1 m HEIGHT



Figure 3
VIEW OF SAMPLING LAYOUT IMMEDIATELY
AFTER EXPLOSIVE DISSEMINATION



Figure 4

SAMPLING LAYOUT SHOWING LIDS BEING PLACED ON
PIE PLATE GROUND CONTAMINATION SAMPLERS



Figure 5

SAMPLING LAYOUT SHOWING COVERED PIE PLATE SAMPLERS
BEING GATHERED AND PLACED INTO CARRYING RACKS



Figure 6

SAMPLING LAYOUT SHOWING PH PLATES IN BACK,
UPWIND READY FOR ALLOCATING

FPP81-1

Figure 1

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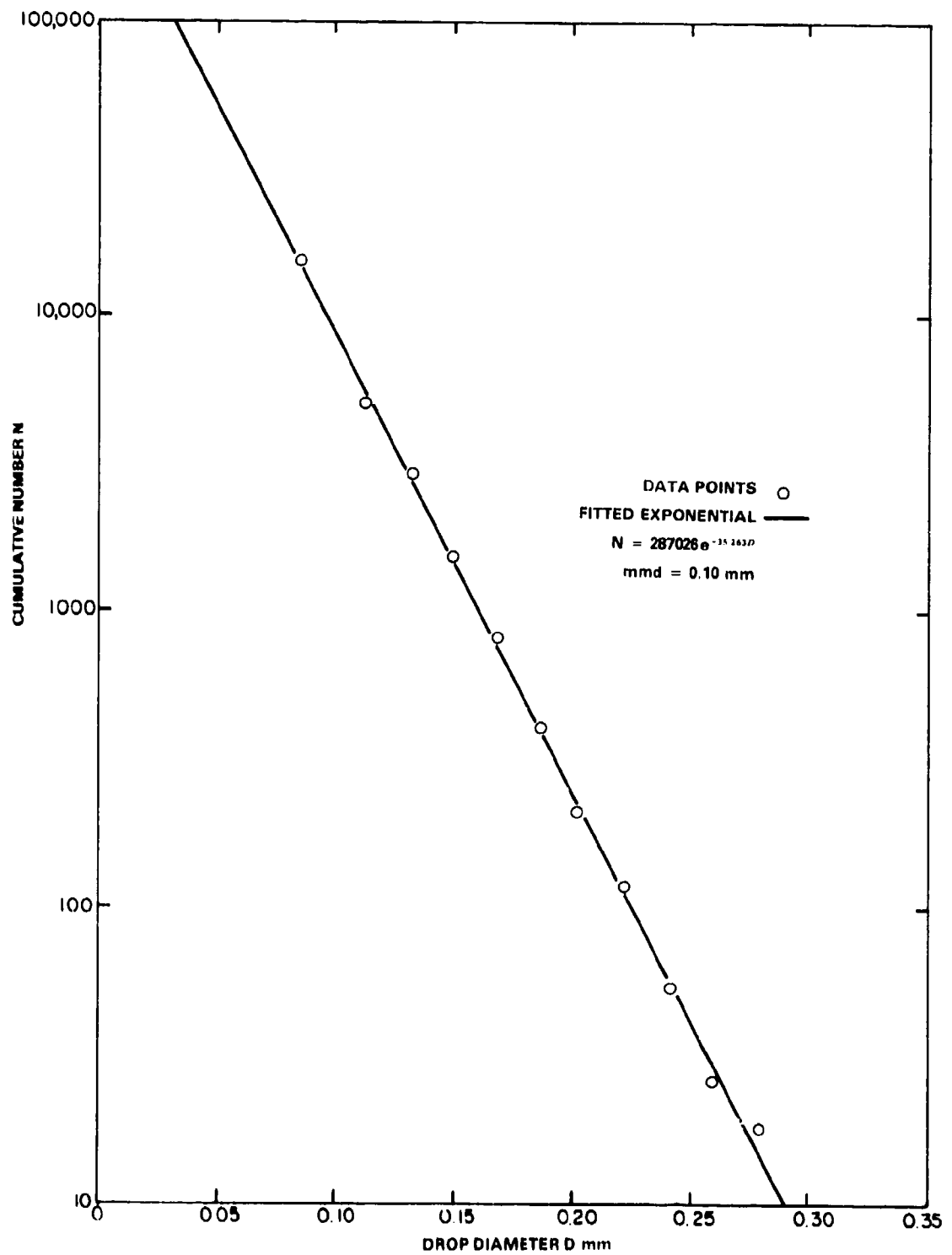


FIGURE 8. DROP DIAMETER-NUMBER DISTRIBUTION FPP 81-TRIAL 1

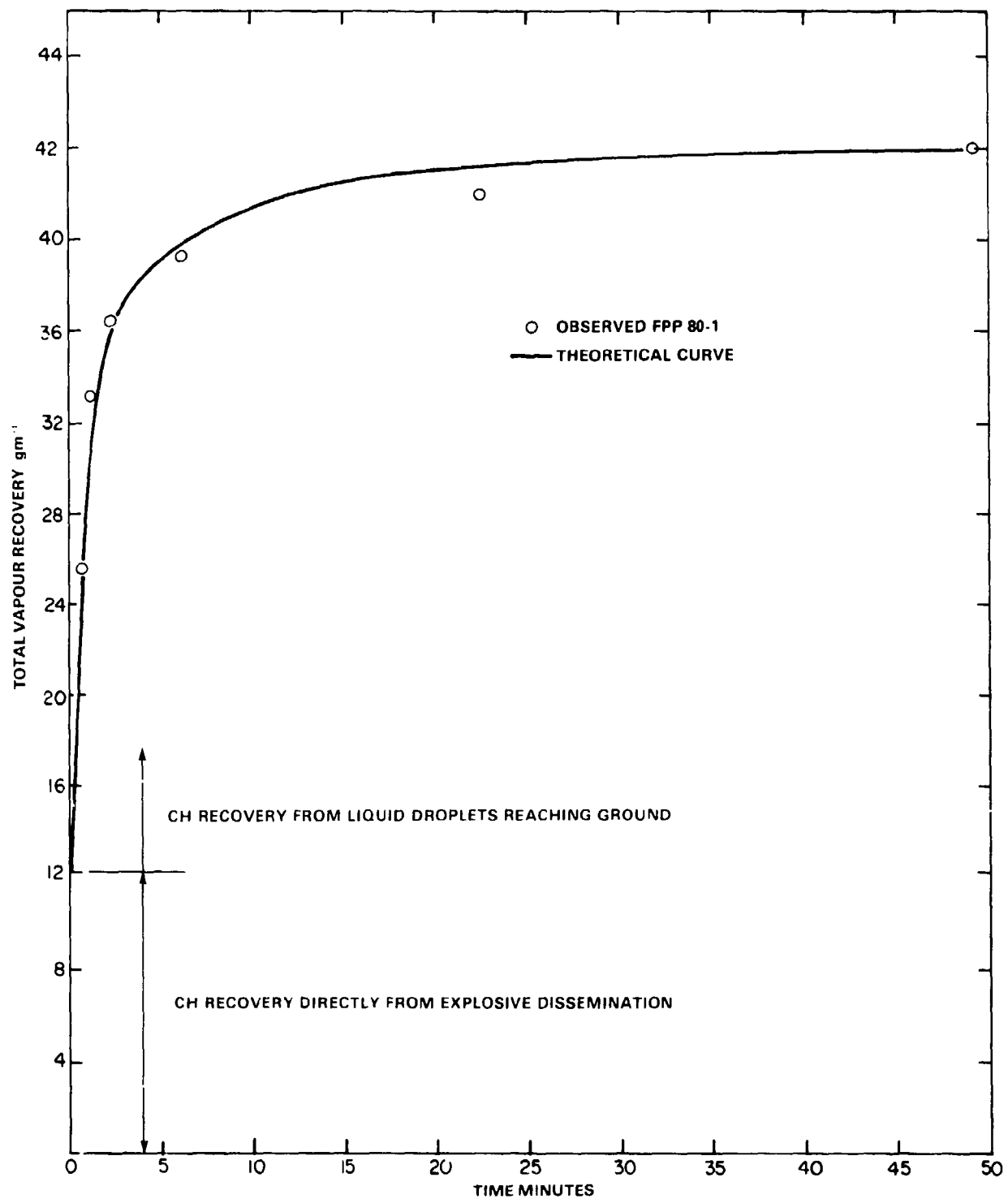


FIGURE 9. VAPOUR RECOVERY DATA ADJUSTED TO GROUND
TEMPERATURE 20°C AND 2 m WINDSPEED 18 km hr^{-1}

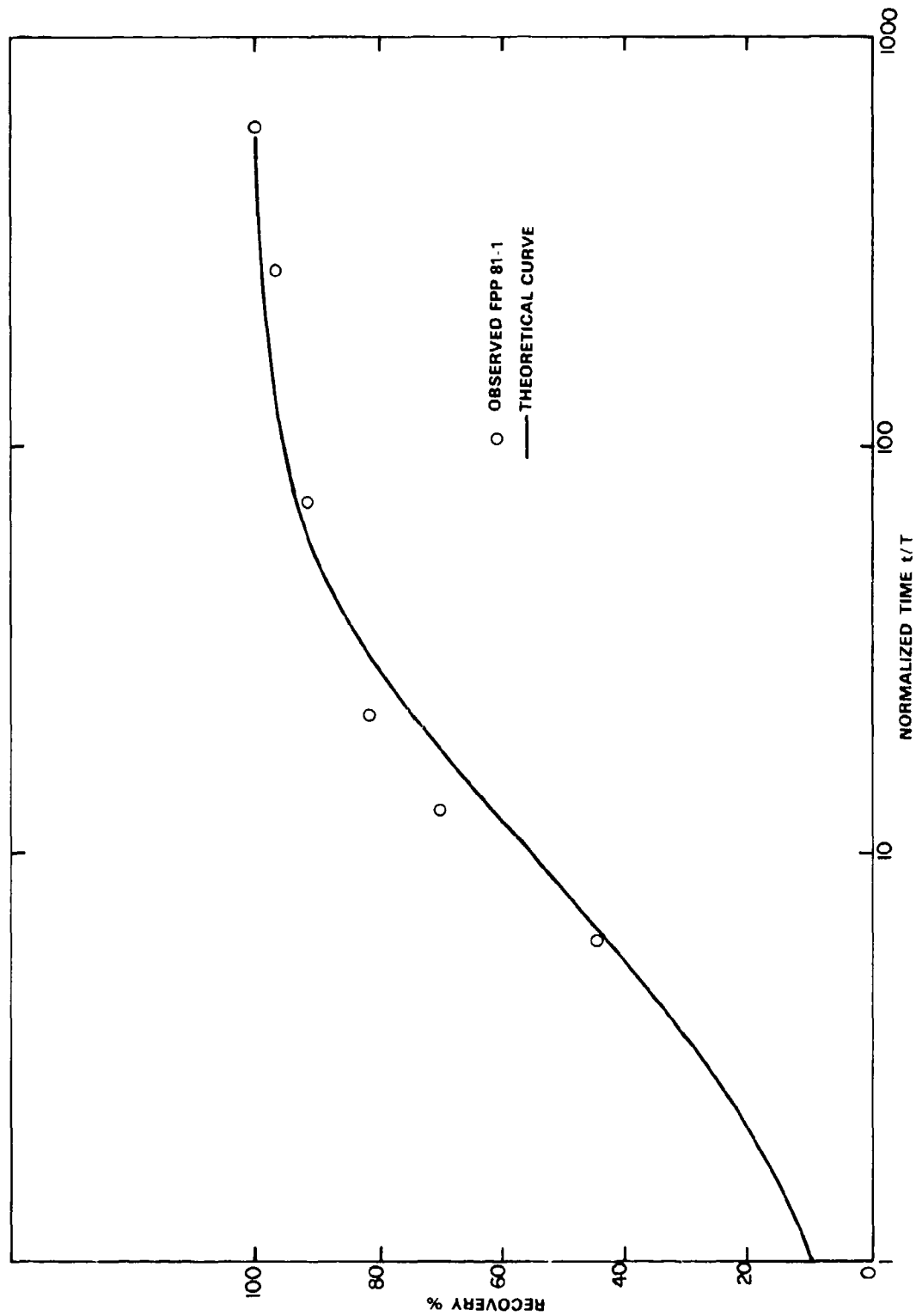


FIGURE 10. NORMALIZED VAPOUR RECOVERY DATA FOR CH FROM GROUND CONTAMINATION

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13. ABSTRACT A trial with CH was conducted on prairie terrain. Explosive dissemination yielded liquid droplets of 0.1. mm mass median diameter. 90% of the total vapour recovery occurred within four minutes and 88% of the disseminated chemical was recovered. ↗ (U)			

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KEY WORDS

VAPOUR
PERSISTENCE
FIELD EXPERIMENT
CHEMICAL SIMULANT
CHEMICAL SAMPLING
EVAPORATION RATE
IRRITANT AGENT

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